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Philipsen, P.H.T.; Baerends, E.J.

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Relativistic calculations to assess the ability of the generalized gradient approximation to reproduce trends in cohesive properties of solids

P. H. T. Philipsen and E. J. Baerends
Theoretical Chemistry Department, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
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We have performed density functional calculations on solids in four columns of the periodic table, containing the elements Ca, Sr, Ba, As, Sb, Bi, Cu, Ag, Au, Ce, and Th. In order to get a meaningful estimation of the quality of the generalized gradient approximation (GGA) to predict trends within a column, as few other approximations were made as possible. Most notably, the spin-orbit effect has not been neglected. In many cases there appears to be a tendency towards underbinding on going down in a column. This is most pronounced in the noble metal column Cu, Ag, Au. The overall performance of the GGA is still reasonable. The mean absolute errors of the calculated cohesive energy, lattice parameter, and bulk modulus are 0.35 eV, 0.10 bohr, and 0.15 Mbar, respectively. Nonnegligible contributions of the spin-orbit coupling are found for the cohesive energy and the lattice parameter of Au and in particular Bi.

I. INTRODUCTION

The local density approximation (LDA) in density functional theory (DFT) has been widely adopted by the solid state physics community.[1–7] This may be explained on the one hand by its relative simplicity and on the other hand by the physicist's familiarity with the electron gas model. The nature of chemistry, however, makes chemists much more demanding in a quantitative sense, and only after the introduction of the generalized gradient approximation (GGA), have they recognized the useful combination of relative simplicity and predictive power of DFT.

The effect of gradient corrections in the solid has attracted considerable attention over the last decade. It is now well established that, similar to the situation in the molecule, first, the lattice is softened: the cohesive energy is reduced, the lattice parameter enlarged and the bulk modulus decreased, and, second, the tendency towards magnetism[8] is increased. The LDA usually overbinding, the softening of the lattice is in the right direction, and the success of a gradient correction depends on the amount of change induced. One of the pioneering investigations on the effect of gradient corrections in the solid state by Bagno *et al.*[9] has shown that the straightforward gradient expansion approximation corrects the LDA much too drastically but that the GGA can certainly compete with the LDA. The GGA outperforms the LDA when it comes to the cohesive energies of Al, C, and Si,[10] and, unlike the LDA, predicts correctly the ferromagnetic bcc ground state for iron.[9] The work of Körling and Häglund[11] on the lattice parameter of transition metals, shows a dramatic improvement for the $3d$ metals, but unfortunately the size of the unit cell is overestimated for the $4d$ and in particular the $5d$ metals. Earlier Barbiellini *et al.*[12] arrived at the same conclusion, based on less systematic work. The improvement of the lattice parameter appears to be reflected in the calculated cohesive energies of the $3d$ metals,[13] as the average error of the LDA of 1.3 eV is reduced to 0.3 eV by the GGA. The structural properties of the sp-bonded solids Al, Si, Ge, are reasonably described by the GGA,[14–16] but the quality of the GGA is not much better than the LDA. Although the cohesive properties[17,18] of the lanthanides are in general improved by the GGA, it has been claimed that the GGA fails to explain the peculiar transition in Ce from the γ to the α phase that both have the fcc structure. According to some[19–21] the transition requires a double minimum in the binding curve, reproduced by neither LDA nor GGA, and the second minimum would be caused by the localization of the f electron that could only be described by self-interaction corrected functionals. This supposedly clear-cut evidence of the failure of the GGA surpasses the fact that only the free energy has to exhibit a double minimum and it has been pointed out[22] that the entropy term stabilizes the Ce lattice most pronounced at larger volumes.

It is fair to conclude that although the GGA is certainly not a uniform improvement over the LDA, it is better on average. At this point in time there does not appear to be a feasible better approximation at our disposal to calculate bulk properties than the GGA. The aforementioned work of Körling and Häglund, however, indicates a systematic tendency of this approximation to increased underbinding going down in a column of transition metals. They have done calculations only at the pseudopotential level, and have therefore only indirectly included relativity. Relativity gaining importance with nuclear charge one might speculate on the impact of this approximation on their results. The question if such systematic errors occur in columns of the Periodic Table makes a proper treatment of relativistic kinematics mandatory. Semirelativistic and scalar-relativistic calculations on bulk systems are common,[23–26] but fully relativistic calculations are not, particularly in combination with the GGA. Fully relativistic LDA calculations on the lattice constant and bulk modulus have been carried out for Pd, Ir, Pt, and Au,[27] but they were not compared to scalar-relativistic calculations. The spin-orbit effect on the bulk energy has been reported for U and Pu,[28] but without the important atomic corrections. Electron localization has been addressed[29] for the actinides by fully relativistic LDA calculations but from the properties under consideration only the

TABLE I. The basis is a mixture of numerical atomic orbitals and Slater type orbitals. The numerical atomic orbitals as well as the frozen core orbitals depend on the electronic configuration used in the numerical spherical atomic program. The configuration is specified in the second column. The third column lists the basis functions, a numerical atomic orbital indicated as NAO and a Slater orbital by its exponent. Orbitals not indicated were kept frozen.

Element	Configuration	Basis
Ca	$[Ar]4s^2$	$3s$(NAO,2.40), $4s$(NAO,0.70,1.65), $3p$(NAO,1.85), $4p$(1.06), $3d$(NAO,1.00), $4f$(1.25)
Sr	$[Kr]5s^2$	$4s$(NAO,2.75), $5s$(NAO,0.75,1.85), $4p$(NAO,1.75), $5p$(1.17), $4d$(NAO,1.25), $4f$(1.25)
Ba	$[Xe]6s^2$	$5s$(NAO,2.70), $6s$(NAO,0.65,1.80), $5p$(NAO,1.55), $6p$(1.22), $5d$(NAO,1.25), $4f$(1.10)
As	$[Zn]4p^3$	$4s$(NAO,1.50.3.30), $4p$(NAO,1.00,2.85), $4d$(1.60), $4f$(1.60)
Sb	$[Cd]5p^3$	$5s$(NAO,1.50.3.40), $5p$(NAO,1.00,2.65), $5d$(1.70), $4f$(1.50)
Bi	$[Hg]6p^3$	$6s$(NAO,1.55.3.55), $6p$(NAO,1.10,2.95), $6d$(1.75), $5f$(2.50)
Cu	$[Ar]3d^{10}4s^1$	$4s$(NAO,0.85,2.45), $4p$(1.00,2.00), $3d$(NAO,1.28,6.90), $4f$(1.50)
Ag	$[Kr]4d^{10}5s^1$	$5s$(NAO,0.90,2.55), $5p$(1.00,2.00), $4d$(NAO,1.45,4.90), $4f$(2.00)
Au	$[Xe]4f^{14}5d^{10}6s^1$	$6s$(NAO,0.95,2.75), $6p$(1.25,2.50), $5d$(NAO,1.55,5.05), $5f$(2.00)
Ce	$[Xe]4f^15d^16s^2$	$5s$(NAO,3.15), $6s$(NAO,0.95,1.65), $5p$(NAO,2.25), $6p$(0.95,1.65), $5d$(NAO,0.95,2.90), $4f$(NAO,1.95), $5f$(1.00)
Th	$[Rn]5f^06d^27s^2$	$6s$(NAO,3.15), $7s$(NAO,1.10,1.90), $6p$(NAO,2.45), $7p$(1.00,2.00), $6d$(NAO,1.05,3.05), $5f$(NAO,1.90,5.70), $6f$(1.35)

bulk modulus was calculated, and was not compared to SR theory.

We present fully relativistically calculated cohesive energies, lattice parameters, and bulk moduli of a variety of systems, ranging from the divalent metals Ca, Sr, and Ba via the pentavalent semimetals As, Sb, and Bi, through the noble metals Cu, Ag, and Au to the rare earth metals Ce and Th. The elements of these four groups lie in the *s*, *p*, *d*, and *f* blocks of the periodic table respectively, and the experimental crystal type is constant within these groups, the only exception being Ba, that has a bcc lattice whereas the other members of the group are of the fcc type. Our aim is to assess the quality of the Dirac-Slater approximation, with the exchange-correlation expression taken from the nonrelativistic GGA. In addition we present the results of scalar-relativistic and nonrelativistic calculations on the same systems thus revealing the scalar-relativistic and the spin-orbit effects, and whether or not they could, in retrospect, have been neglected.

II. DETAILS

The relativistic calculations were performed in the zeroth order regular approximation (ZORA).[30] Details of the implementation of this method in our bandstructure code[31] can be found in an earlier work.[32] In this context it suffices to say that it is an accurate approximation to the Dirac equation. We have employed the parametrization of Vosko and coworkers of the LDA correlation energy.[33] The GGA employs Becke's correction for the exchange energy[34] and Perdew's correction for the correlation energy.[35] In the bulk calculations the GGA energy was evaluated at the LDA density rather than the GGA density, which has been shown to be an excellent approximation.[36] We have neglected relativistic corrections to the XC functional, which is reasonable because it has been shown[37] that this affects bonding energies by 0.05 eV and bond lengths by 0.01 bohr. The calculation of the atomic corrections was done by minimizing the energy according to Ref. 38. The procedure is started by converging a certain configuration. If the self-consistent solution has incompletely filled levels below the Fermi level, charge is transferred from the Fermi level to these states, and the corresponding configuration is again converged. This cycle is repeated until Aufbau is reached with possibly fractional occupations at the Fermi level. We have done this procedure without symmetry constraints on the density. In open shell systems both the spin-polarization and the spin-orbit effects can be important. The inclusion of spin-polarization in spin-orbit calculations can be done[39] by using the relative size of the magnetization vector as the spin-polarization

$$\zeta = |\vec{m}|/\rho, \tag{1}$$

with the magnetization vector

$$\vec{m} = \mathrm{Tr}\, \underline{\underline{\vec{\sigma}}}\, \underline{\underline{\rho}}, \tag{2}$$

where ρ is the 2×2 spin density matrix. This model has been used in the study of noncollinear magnetism.[40,41] We have used the *z* component of the magnetization vector only, leading to

$$\zeta = \rho_{\alpha\alpha} - \rho_{\beta\beta}. \tag{3}$$

To obtain the equation of state for the three elements with a hexagonal close-packed lattice (As, Sb, Bi) we have kept the so-called c/a-ratio at the experimental value, rather than optimizing this ratio at each sampled lattice constant.

We now discuss more technical details. The integration over reciprocal space was done with the analytical quadratic method.[42] The number of symmetry unique *k* points in the irreducible wedge of the Brillouin zone for the face-centered cubic, body-centered cubic, and rhombohedral crystals were 175, 84, and 316, respectively. A numerical Gaussian integration scheme[43] was employed to evaluate matrix elements of the Hamiltonian, and the points were chosen such that the error of typical integrals was less than 10^{-5}. The basis sets, constructed from linear combination of atomic orbitals, are shown in Table I. The atomic orbitals can be either numerical atomic orbitals (NAO's) or Slater-type orbitals (STO's). As can be seen from the table a valence orbital of an atom is

TABLE II. Maximum absolute error, due to several approximations, in E (eV), a (bohr), and B (Mbar) for scalar-relativistic calculations on the test set Sr, Ba, Sb, Ag, and Ce. Details on the test calculations are given in the text. The last row gives an estimation of the overall accuracy, assuming independent errors.

Approximation	ΔE	Δa	ΔB
k-space sampling	0.02	0.04	0.03
Finite basis set	0.02	0.02	0.07
Binding curve description	0.00	0.00	0.01
Numerical integration	0.00	0.01	0.01
Overall accuracy	0.03	0.05	0.08

described by the corresponding NAO, that gives a proper description of the valence function in the core region, and, for additional freedom, two STO's with exponents such that one of them is more contracted than the NAO and the other is more diffuse. We have added polarization orbitals with angular momenta up to $l=3$. In cases where the numerical atom had a virtual orbital energetically close to the highest occupied orbital we have added this unoccupied NAO to the basis set, as for instance, the $3d$ orbital of Ca and the $5f$ of Th. In general the frozen core was kept very small to rule out any significant effect of this approximation. Only in the series As, Sb, Bi the core was chosen slightly larger, but still reasonably small, because these solids have the rhombohedral lattice structure that has two atoms per unit cell and are more expensive to calculate. The binding curve in the vicinity of the minimum was obtained as the interpolating parabola in three equidistant points bracketing the minimum, with a spacing of 0.2 bohr. For the rhombohedral crystals the angle α was kept fixed at the experimental values as tabulated in Ref. 44. The density was expanded in an auxiliary basis set in order to evaluate the Coulomb potential and the gradient of the density. We have ensured enough flexibility in both the radial and angular degrees of freedom, such that the least-squares error norm of the fitted density was well below 0.01 electrons. For Ce and Th it was important to include h and i functions.

Table II provides information on the accuracy of our calculational procedure for which we have performed additional test calculations at the scalar-relativistic level on a subset of the systems considered in this article. The test set included Sr, Sb, Ag, Ce, thus covering the four columns with one representative element, and was completed with Ba because it is the only studied element with a bcc lattice. For these five elements we have examined the influence of the four most important calculational approximations being the k-space sampling, the finite basis set, the binding curve description, and the numerical integration. To check the appropriateness of the employed k-space sampling we have repeated the calculations with a better sampling such that for all lattice types — fcc, bcc, and hcp — the number of sampling points was more than doubled. The quality of the basis sets was estimated by comparing the results to the outcomes with larger basis sets. The larger basis sets were constructed from the original basis sets by adding one STO to the atomic shell descriptions of the valence and polarization levels, keeping the core orbitals and the NAOs fixed. In atomic shell descriptions comprising one STO this orbital was replaced by two orbitals of this type, one 10% more contracted and the other 10% more diffuse than the original STO. In case of two STOs these two orbitals were replaced by one STO that was 10% more contracted than the most contracted original STO, a second STO 10% more diffuse than the most diffuse original STO and a third STO with its expectation value of the radius in between. Counting the NAOs, valence electrons were thus described at a ''quadruple-ζ'' level. The correctness of our procedure to obtain the binding curve near the minimum as the interpolating parabola in three calculated points spaced 0.2 bohr, was checked with an alternative method to fit the parabola to five equidistant points spaced 0.1 bohr. Finally the numerical integration mesh was substituted by one with typically 60% more points, integrating characteristic integrals one order of magnitude better. From the table we see that two largest approximations are the k-space sampling and the basis set. If we assume that the approximations are uncorrelated, the energy has an accuracy of about 0.03 eV, the lattice constant has an uncertainty of ~ 0.05 bohr and the bulk modulus is reliable up to ~ 0.08 Mbar.

TABLE III. Cohesive energies according to the three theoretical models, with the atomic corrections as specified in Table VI. The last line contains the mean absolute error (MAE).

Element	NR	SR	FR	Expt.
Ca	1.71	1.67	1.67	1.84
Sr	1.52	1.37	1.37	1.72
Ba	2.07	1.65	1.66	1.90
As	2.66	2.65	2.63	2.96
Sb	2.52	2.47	2.42	2.75
Bi	2.35	2.32	1.81	2.18
Cu	3.12	3.30	3.30	3.49
Ag	2.12	2.36	2.37	2.95
Au	2.11	2.84	2.99	3.81
Ce	3.22	4.21	4.16	4.32
Th	5.09	6.05	5.93	6.20
MAE	0.57	0.32	0.35	

III. RESULTS

The calculated cohesive energies, lattice parameters, and bulk moduli are shown in Table III, Table IV, and Table V, respectively. In these three tables nonrelativistic, scalar-relativistic, and fully relativistic numbers are shown. We will first look at the FR outcomes to judge the quality of the GGA, then discuss the roles played by the scalar-relativistic and spin-orbit effects, subsequently take a closer look at the atomic corrections, and finally summarize the main conclusions.

A. Performance of the GGA

The fully relativistic cohesive energies from Table III match in most cases reasonably with experiment. The 0.35 eV mean absolute error of the GGA is only slightly worse than the 0.3 eV error for the $3d$ transition metals.[13] In all cases the cohesive energy is underestimated. The errors in

TABLE IV. The lattice constant (bohr) as calculated with the three theoretical models. The last line contains the mean absolute error.

Element	NR	SR	FR	Expt.
Ca	10.39	10.39	10.39	10.54
Sr	11.33	11.30	11.30	11.49
Ba	9.36	9.44	9.44	9.49
As	7.72	7.72	7.72	7.80
Sb	8.57	8.56	8.56	8.52
Bi	9.13	9.02	9.12	8.98
Cu	6.95	6.88	6.88	6.82
Ag	8.07	7.88	7.88	7.73
Au	8.41	7.91	7.88	7.71
Ce	8.52	9.00	9.02	9.03
Th	8.70	9.58	9.59	9.60
MAE	0.30	0.09	0.10	

the ''*s* column'' Ca, Sr, Ba are -0.17, -0.35, and -0.24, thus not perfectly reproducing the trend in the experimental numbers. The LDA error for Ca is 0.4 eV,[45] larger than the GGA error for this element. In the ''*p* column'' with the elements As, Sb, and Bi the errors are more constant: -0.33, -0.33, and -0.37, and the experimental trend is well preserved. The results are the worst for the noble metals. In the ''*d* column'' Cu, Ag, Au the errors are -0.19, -0.58, and -0.82. The 0.8 eV underestimation for Au leads to the largest error in the total set, and the calculated E_0 of Au is 0.3 eV smaller than the E_0 of Cu, at variance with the empirical fact that it should be 0.3 eV larger. It is known[25] that the LDA predicts the cohesive energy of Au accurately, but the LDA probably spoils the trend even more because according to the semirelativistic calculations of Ref. 25 the LDA E_0 of Au is 0.9 eV less than the one for Cu. In the series of the dimers of the three noble metals the calculated[30] FR atomization energies are in much better accord with experiment. Nevertheless in the errors 0.14, 0.05, -0.05, the same propensity towards underbinding on going down in a column is visible, albeit much smaller. The GGA performs remarkably well for the ''*f* column'' Ce and Th, the errors -0.16, and -0.27 being small compared to the large formation energies of these elements. In all four columns the underbinding of the heaviest element is larger than the underbinding of the lightest element.

TABLE V. The bulk modulus (Mbar) as calculated with the three theoretical models. The last line contains the mean absolute error.

Element	NR	SR	FR	Expt.
Ca	0.17	0.17	0.17	0.15
Sr	0.12	0.11	0.11	0.12
Ba	0.09	0.08	0.08	0.10
As	0.76	0.76	0.76	0.39
Sb	0.50	0.50	0.55	0.38
Bi	0.38	0.45	0.44	0.32
Cu	1.37	1.26	1.26	1.37
Ag	0.62	0.80	0.80	1.01
Au	0.71	1.32	1.30	1.73
Ce	0.59	0.33	0.32	0.35[a]
Th	1.07	0.67	0.66	0.54
MAE	0.25	0.14	0.15	

[a]Reference 47.

The mean absolute error of the GGA for the lattice parameter, see Table IV, is 0.1 bohr. The lattice parameters in the series Ca, Sr, Ba are all underestimated, the errors being -0.15, -0.19, -0.05. In the series As, Sb, Bi the calculated lattice parameter changes gradually from too small to too large as can be seen from the errors -0.08, 0.04, 0.14. For the noble metals the lattice constant of Cu is already overestimated by 0.06 bohr and the overestimation increases via 0.15 bohr for Ag to 0.17 bohr for Au. Again the error for Au is the largest in the total set. The LDA underestimates the lattice constant of Au by 0.06 bohr.[27] In the corresponding dimer series as calculated in Ref. 30 the interatomic distance has the errors -0.02, 0.06, 0.08, exhibiting a similar trend as in the bulk. The lattice parameters of Ce and Th are predicted within the accuracy of the calculations. In two of the four columns there is a growing tendency to overestimate the lattice constant. In the column with Ca this is true if the first and the last row are compared.

From Table V we see that the mean absolute error of the bulk modulus is 0.15 Mbar. In the Ca column the errors are within the accuracy of the calculation. The situation is markedly different in the As-headed column, the errors in the bulk modulus being 0.36, 0.11, and 0.06, the elasticity of the solids changing gradually from much too small to more elastic values. In the Cu, Ag, Au series the errors are -0.11, -0.21, -0.44: the bulk modulus is already too small for Cu and the underestimation grows gradually in this column. In the corresponding dimer series the calculated vibrational energy also shows a growing underestimation given the errors 7, -9, -17 cm^{-1}. The errors of Ce and Th are -0.03 and 0.12 and in this case the trend is reversed.

B. Relativistic effects

Now we proceed with a discussion of the role played by relativity in our calculations. In the *s*-column Ca, Sr, Ba, the scalar-relativistic effects on the (positive) cohesive energy are -0.04, -0.15, and -0.41 eV. The scalar-relativistic effect reduces the cohesive energy increasingly in this column. The lattice parameter is unaltered by this effect except for the 0.14 bohr expansion of the Ba lattice, and the bulk modulus is unaltered for all three elements. No significant changes are induced by the spin-orbit coupling in this column. In the *p* column As, Sb, Bi, the cohesive energy is remarkably insensitive to the scalar-relativistic effect. The lattice parameter is reduced 0.16 bohr for Bi. The spin-orbit effect reduces the Sb cohesive energy 0.09 eV and has no effect on the lattice parameter of this material. The calculated properties of the element Bi exhibit the most spectacular contributions of the spin-orbit coupling. The cohesive energy is reduced 0.56 eV. Note that our conclusion that the trend of the cohesive energy in the *p* column is well predicted by the GGA depends critically on this large correction. The lattice parameter is expanded 0.1 bohr by this effect. The bulk modulus is not changed significantly in this column by the

TABLE VI. The nonzero atomic corrections (eV) in the three theoretical models. The ground state energy of an atom is the energy of the spherical spin restricted atom in the configuration as specified in Table I minus the atomic correction.

Element	NR	SR	FR
As	1.66	1.66	1.68
Sb	1.39	1.40	1.49
Bi	1.29	1.32	2.20
Cu	0.26	0.26	0.26
Ag	0.22	0.22	0.22
Au	0.20	0.20	0.20
Ce	3.69	1.40	1.50
Th	7.43	0.78	1.01

two relativistic effects. A similar weakening of the bond is also seen in the Bi dimer because the spin-orbit coupling decreases the formation energy 0.76 eV and increases the bond length 0.06 bohr in this molecule.[46] The scalar-relativistic effect cannot be neglected throughout the *d* column Cu, Ag, Au. The cohesive energy of Cu is already increased by 0.19 eV. For Ag and Au the numbers are 0.23 and 0.73, respectively. The effects on the lattice parameter in this column are -0.06, -0.18, and -0.52. Also for the bulk modulus the scalar-relativistic effects -0.11, 0.18, and 0.62 are non-negligible. The spin-orbit coupling only affects the properties of Au, reducing the cohesive energy by 0.16 eV and contracting the lattice by 0.03 bohr. The spin-orbit effect in the bulk is different from the effect in the Au dimer,[46] because in the dimer the formation energy is unchanged by the spin-orbit coupling. The bond length of the dimer, however, is contracted similarly 0.01 bohr. The most dramatic scalar-relativistic effects are seen in the *f* column. The cohesive energy is increased roughly by one eV for both elements. The Ce lattice is expanded by 0.53 bohr and the Th lattice by 0.85 bohr. The excellent performance of the GGA for these elements would not have been apparent neglecting the relativistic effect. The spin-orbit coupling reduces the cohesive energy of Ce 0.05 eV, and for Th the reduction is 0.11 eV. The lattice parameter is essentially unaffected.

C. Atomic corrections

The atomic corrections, presented in Table VI, play a significant role in the determination of the cohesive energy. As explained before they result from an optimization of the occupation numbers without symmetry constraints on the density. In the FR case, only for Ce we have found the final solution to have two fractionally occupied orbitals (spinors) at the Fermi level, each occupied with half an electron, all other FR atoms have integral occupation numbers. The atomic correction for the noble metals is due to the spin-polarization of the *s* electron. For As, Sb, and Bi the valence *p* occupation is three. In this series we see the competition of the spin-polarization against the spin-orbit effect at work. Nonrelativistically these atoms have three spin-parallel valence *p* electrons. Transforming the basis of spin orbitals ($p_x\alpha$, $p_x\beta$, etc.) to a basis of $p_{1/2}$ and $p_{3/2}$ spinors, this can be shown to correspond to a $p_{1/2}$ population of 1 and (of course) a polarization charge of 3. In the FR As atom the $p_{1/2}$ occupation is 1.12 and the polarization charge is 2.98. The $p_{1/2}$ population increases to 1.34 for Sb, whereas the polarization charge decreases to 2.90 for this element. In Bi the numbers deviate further from the nonrelativistic values as the $p_{1/2}$ occupation becomes 1.84 and the polarization charge reduces to only 1.99.

The rare earths Ce and Th have complicated ground states. Due to the near degeneracy of the valence *s*, *d*, and *f* orbitals, a mixing of these orbitals takes place as can be seen from the $6s^{1.85}5d^{0.65}4f^{1.5}$ and $7s^{1.91}6d^{1.82}5f^{0.26}$ configurations that we have found for Ce and Th.

In the NR and SR models the ground states are simple but for Ce and Th. The SR configurations for Ce and Th ($6s^{1.92}5d^{0.51}4f^{1.56}$ and $7s^{1.90}6d^{1.70}5f^{0.41}$) are similar to the FR case, but nonrelativistically the *f* orbital is much more favored as is visible in the $6s^{1.74}5d^{0.26}4f^{2}$ and $7s^{1.63}6d^{0.07}5f^{2.3}$ configurations that we have found. The destabilization of the contracted *f* orbital is the main relativistic effect which explains the huge expansion of the lattice that the SR effect brings about for these elements.

D. Conclusions

In conclusion, from all three calculated properties the picture emerges that the GGA tends to underbind the crystal on going down in a column: cohesive energies are increasingly underestimated, lattice parameters overestimated, and bulk moduli underestimated. This effect is worst for the noble metals Cu, Ag, Au, and this particular failure of the GGA demands the development of an improved functional. As a smaller yet qualitatively similar effect is visible in the corresponding dimer series, the testing of an alternative functional might well be done initially on these, readily calculated dimers. As opposed to the noble metals, the rare-earths Ce and Th are remarkably well described by the GGA. Scalar-relativistic effects are largest in the Ce, Th column, and the effect can be understood by the atomic-configuration change due to the destabilization of the valence *f* orbital. Another noticeable SR effect is seen for Au. As expected, the spin-orbit effect is largest for the element at the bottom of the *p* column, Bi, affecting particularly the cohesive energy by a reduction of 0.6 eV, and expanding the lattice by 0.1 bohr. Also the cohesive properties of Au are somewhat sensitive to the spin-orbit effect, but the effect can be safely neglected for the other materials.

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